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NEUTRAL AND ACID PRODUCTS OF THE INTERACTION OF ISOOCTANE WITH DILUTE NITRIC ACID

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Following is a summary of two articles (1,2) by the above authors. It represents a supplement to another article (3) by the same authors, since it deals with work basic to that investigation.

Relationships underlying the nitration of saturated hydrocarbons are of importance because the resulting nitro derivatives may serve either as additives to Diesel fuels, which improve the performance of the latter, or as monopropellants for rockets. Results clarifying the mechanism of the oxidation of low-boiling hydrocarbons with nitric acid, or with intermediate products formed in the course of a combined nitration and oxidation, may also conceivably be utilized in work on rocket bipropellants.

Despite the fact that isooctane (2,2,4-trimethylpentane), is produced commercially and is widely used, its chemical properties have been studied very little. Substantially, it must be studied by comparing its properties with those of trimethylethylmethane and trimethylpropylmethane, compounds of similar structure which V. V. Markovnikov (4) had begun to investigate, and also on the basis of certain very recent works on the cracking of isooctane (5).

Of particular interest are those interactions which lead to a significant decomposition of isooctane. In what directions does such a decomposition proceed, what are its intermediate stages, and what is the interrelation between the different direction of the reaction?

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In the case of the interrelation between oxidation and nitration the above questions have been thoroughly studied (6) for aromatic hydrocarbons with aliphatic side chains and for monocyclic and bicyclic naphthenes, but very inadequately, as applied to paraffins in general, and in particular, as far as isoparaffins containing a quaternary carbon atom are concerned. This interrelation in the case of isooctane is the subject of the present investigation.

Isooctane C_8H_{18} (bp 99.4-99.5°) was nitrated by Konovalov's method in sealed tubes, with nitric acid having a specific weight of 1.075. The mixture was heated at 143-147° for 20 hr, after which the upper oily layer was separated from the lower acid layer, and the two analyzed separately.

The neutral products in the oil portion were separated by fractional distillation (up to 110° at normal pressure, then at 36 mm up to 95°). All products which boiled over 95° at 36-mm pressure, together with the distillation residue, were subjected to treatment with alkali under heat to separate out nitro compounds of isooctane.

Those neutral products which boiled at up to 95° at 36 mm comprise the following:

Isooctane $(CH_3)_3C \cdot CH_2 \cdot CH \cdot (CH_3)_2$. The initial isooctane which did not enter into the reaction was the chief product by weight, amounting to a little less than half of the quantity of the original reagent.

Nitromethane CH_3NO_2. Could not be separated from isooctane due to the fact that its boiling point (100.8-100.9° at 760 mm) is close to that of isooctane. Was determined qualitatively by its reaction for alkylnitrolic acid in an alkaline extract of the 97-103° fractions, and by its Manzoff (7) reaction in a water-ammonia extract of the same fractions.

2,24-dimethylpentanone-4 $(CH_3)_3C \cdot CH_2 \cdot CO_2CH_3$. A small quantity, with a boiling point of 125.5-126°, was produced. Its constants correspond to published data (8). Its formation is closely tied in with the formation of nitromethane.

2,24-trimethylpentanone-3 $(CH_3)_3C \cdot CO \cdot CH(CH_3)_2$. A small quantity was formed as a result of the decomposition of secondary isonitroisooctane which was formed intermediately (bp 133.5-135° at 759 mm). Its constants correspond closely to published data (9).

Acetone $CH_3 \cdot CO \cdot CH_3$. A small quantity was discovered in the first fractions of the water-acid layer from the nitration of isooctane.

After the light neutral products had been driven off, the residue was treated with a strong aqueous solution of caustic alkali. The following were obtained: an aqueous alkaline solution, into which secondary nitroisooctane would have to pass; and an oil insoluble in the alkali, which was substantially tertiary nitroisooctane. Both these nitroisooctanes were isolated in a pure form.

Secondary nitroisooctane $(CH_3)_3C \cdot CH(NO_2) \cdot CH(CH_3)_2$. A small quantity of this heavy, slightly yellowish oil was obtained (bp 69-71° at 5 mm).

Tertiary nitroisooctane $(CH_3)_3C \cdot CH_2 \cdot C(NO_2)(CH_3)_2$. This principal component of the neutral oil, which was insoluble in the alkali, was obtained in a substantial quantity after two distillations in vacuum. It was a colorless oil with a bp of 100.4° at 34.5 mm. The constitution of tertiary nitroisooctane is determined by the structure of the original isooctane, which contains only one tertiary hydrogen. It is interesting that 2,2-dimethylpentanone-4

(see above) was detected when tertiary nitroisooctane was heated with water. The chemistry of the latter-transformation should form the subject of a special investigation.

Dinitroisooctane $(CH_3)_3C \cdot CH(NO_2) \cdot C(NO_2)(CH_3)_2$. Obtained by fractionation of the residue after the separation of tertiary nitroisooctane, this high-boiling, light yellow oil was obtained in a small quantity (bp 124-124.5° at 21.5 mm). It is insoluble in aqueous alkali even when heated, but dissolves in an alcoholic solution of alkali when cold, with appearance of yellow color and the precipitation of crystals. The alkaline solution of this dinitro compound's salt produces a characteristic pseudonitrol reaction, and consequently one of its nitro groups has a secondary character; the second nitro group, as it appears from the structure of isooctane, is obviously tertiary. Thus, the structure of dinitroisooctane is determined as 2,2,4-trimethyl-3,4-dinitropentane.

The acid layer from the interaction of isooctane with dilute nitric acid was subjected to steam distillation, which was stopped once the acidity became negligible. The distillate was neutralized with sodium bicarbonate to a weakly alkaline reaction and again subjected to steam distillation to remove any light neutral products remaining, such as acetone and nitromethane. The neutralized distillate was then evaporated to a small volume, acidified with sulfuric acid, using tropeolin paper as an indicator, and again subjected to steam distillation. Now the first rough separation of monobasic fatty acids into the simplest (from C_1 to C_4), easily soluble in water, and into the higher molecular (beginning with C_5), which are soluble with difficulty in water, was obtained.

Further identification was made by the following methods:

1. The microchemical characteristics of the salts.

2. Preparation of the p-phenylphenacyl esters of indivdual acids or of their simple mixtures, and the characterization of these esters.

3. The physicochemical characteristics of the individual acids (boiling point, melting point) after their careful fractionation.

4. Determination of the molecular weight of the individual acids through their titration and in some cases their elementary analysis.

The composition of the acid layer was as follows:

Monobasic acids from C_1 to C_4. Part of the last distillate, containing the water solution of lower fatty acids, was neutralized with calcium hydroxide and evaporated to dryness in a water bath. Part of the resulting mixture of solid calcium salts was separated further by treatment with absolute ethyl alcohol on a water bath under heating and stirring.

The insoluble precipitate contained only calcium acetate (typical octahedra of sodium uranylacetate were obtained). The alcohol solution was found after evaporation to contain only isobutyric acid.

Monobasic acids from C_5 to C_6. These acids after steam distillation formed an oily layer on the surface of the distillate. Water was removed with anhydrous sodium sulfate, and the mixture was fractionally distilled. The two basic fractions boiled at 162-164° and 181-183°. The former contained trimethylacetic acid, and the latter tertiary butylacetic acid.

Dibasic acids. The residue after the distillation of neutral products and volatile acids from the acid layer was evaporated in a water bath to a small volume and cooled. White crystals formed. This residue was found to contain alpha, alpha-dimethylsuccinic acid and traces of oxalic acid.

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